

CHARACTERIZATION OF OZONE PRECURSOR EMISSIONS FROM COAL FIRED POWER PLANTS AND THEIR IMPACTS

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A technical report submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Environmental Sciences and Engineering in the Gillings School of Global Public Health.

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ABSTRACT

Kesava Anirudh Vajjala: Characterization of Ozone Precursor Emissions from coal fired power plants and their impacts
(Under the direction of William Vizuet)

Ground level ozone is generated due to chemical reactions between species such as NO_x and VOCs in the presence of sunlight. Coal fired power plants are known to be significant sources of NO_x, VOCs, and other species. The electricity produced by coal fired power plants contributed to about 39% of the nation's energy production in 2014. Emissions from coal fired power plants will lead to increased ozone production.

Emission data from 80 coal fired power plants in the eastern United States was used to analyze their impacts on ozone levels. The CAMx model was used to predict the impact on ozone concentrations when NO_x emissions from these power plants were reduced. The emissions were removed or zeroed out 24 hours prior to the start of measurement. Over the majority of the domain, the model predicted that there was a decrease in hourly ozone concentrations of more than 10ppb and increases of up to 8ppb. There are 11 nonattainment areas for ozone in the eastern United States. In all these regions ozone concentrations were reduced by 1ppb to 10ppb, and increased by 1ppb to 5ppb.

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LIST OF ABBREVIATIONS

ARP – Acid Rain Program

CAIR – Clean Air Interstate Rule

CAMx – Comprehensive Air Quality Model

EGM – Electricity Grid Management

EGUs – Electricity Generation Units

EPA – Environmental Protection Agency

LNB – Low NO_x Burners

NAAQS – National Ambient Air Quality Standards

NBP – NO_x Budget Trading Program

SCR – Selective Catalyst Reduction

SNCR – Selective Non Catalyst Reduction

VOCs – Volatile Organic Compounds

CHAPTER 1: PROBLEM IDENTIFICATION BRIEF

Introduction

Ozone was classified as a criteria air pollutant in 1971, by the U.S Environmental Protection Agency (EPA). Ozone is a common urban air pollutant with known adverse health effects ranging from respiratory symptoms to increased risk for hospital admissions. The U.S Environmental Protection Agency (EPA) established primary National Ambient Air Quality Standards (NAAQS) for ozone and other criteria pollutants at a level intended to protect human health with an adequate margin of safety (1). As of 2015, the U.S EPA proposed that the daily 8-hour standard be 70ppb.

Climate and Health Impacts of Ozone

Ozone is a gas that is produced in the atmosphere as a result of chemical reactions. There are no direct sources of ozone. Ozone's impact on climate consists primarily of changes in temperature. The more ozone in a given parcel of air, the more heat it retains. Ozone generates heat in the stratosphere, both by absorbing the sun's ultraviolet radiation and by absorbing upwelling infrared radiation from the troposphere. This "heating effect" causes the temperature of the earth's surface to rise.

Due to its high oxidizing potential, ozone causes damage to mucous and respiratory issues in living organisms. This makes ozone a potent respiratory hazard and pollutant near the ground level. (2) Many health effects of ozone involve lung-cancer, labored breathing, etc.

There is a great deal of evidence to show that ground level ozone can harm lung function and irritate the respiratory system. Exposure to ozone and the pollutants that produce it

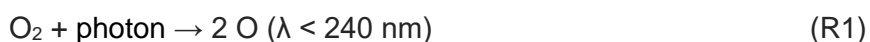
are linked to many other adverse health outcomes such as premature death, asthma, bronchitis, heart attack and other cardio pulmonary problems. (3)

There are studies showing that ozone can lead to a multitude of illnesses and increased susceptibility to other diseases such as bronchitis, pulmonary fibrosis, etc. (4). Another study of 450,000 people living in the US cities saw a significant correlation between ozone levels and respiratory illness over the 18-year old follow up period. The study revealed that people living in cities with high ozone levels such as Houston or Los Angeles had an over 30% increased risk of dying from lung disease. (5)

Ozone chemistry

Ozone is found most in the stratosphere, between 10km and 50km above the surface of the earth. Ozone in the stratosphere is mostly produced from UV rays between wavelength of 240 and 169nm.

Ozone is created and destroyed by a series of chemical reactions called the Chapman Mechanism, as shown in reactions R1, R2 and R3.



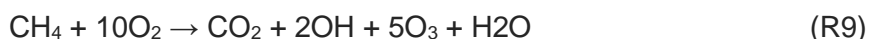
Tropospheric ozone is an atmospheric pollutant. It is not emitted directly from any source, but is formed by the reaction of sunlight on air containing hydrocarbons and nitrogen oxides that react to form ozone directly at the source of the pollution or some distance down wind.

Ozone reacts directly with some hydrocarbons such as aldehydes and other compounds. The lifetime of the tropospheric ozone is about 22 days; its main removal

mechanisms are being deposited into the ground and reactions with compounds such as OH, hydroxyl radical (HO•) and peroxy radical (HO₂•). (6)



Ozone is also formed from reactions involving NO_x (NO and NO₂) and HO_x (H, OH and HO₂) species, as shown in reactions R6, R7, R8 and R9.



Ozone production increases linearly with hydrocarbon concentrations, but varies inversely with NO_x concentrations in a VOC limited regime. It is called as a VOC limited regime as the O₃ production rate is limited by the supply of the VOCs.



Due to the inverse relationship between O₃ and NO_x in a VOC limited regime, more ozone is generated when there is a decrease in NO_x. In the immediate vicinity of large emissions of NO from point-sources such as power plants, ozone concentrations are depressed through a process called NO_x titration. This consists of the removal of ozone through reaction with NO, as shown in R12.

This was a worry for the regulators due to the intricate nature of these ozone generating mechanisms. Thus, NO_x and VOCs are major sources of ozone.

Electrical Generation Units and Coal fired power plants

Electricity generation units (EGUs) are important sources of nitrogen oxides (NO_x) that contribute to ozone. EGUs have been growing every year in the US since 1950 and is projected to grow by another 20% by 2040. (7)

Nearly 70% of all the net electricity generation in the US during 2011 was from fossil-fuel sources, with 43% of that electricity produced from coal combustion. (8)

During the combustion process in an EGU, NO_x and various other pollutants are formed and emitted. As of 2008, EGUs account for 19% of all anthropogenic NO_x emissions in the US, 90% of which was a product of electricity generation from coal. (9)

EGUs work by using coal to boil water (involves coal combustion) and burning natural gases in a turbine, where the turbines are driven by combustion processes. Combined cycles involve generating electricity by burning coal to drive steam and natural gases into the turbine. From these combustion processes, a significant amount of pollutants are emitted, including NO_x.

The NO_x emissions from EGUs have a seasonal trend within the US – they have increased emissions between summer and winter. This is due to the increased temperatures in the summer season. And in general, the NO₂ productions in the summer have been observed to be more than that of those in the winter season. (10)

Though there has been a gradual decrease in the dependency on coal combustion for electricity generation, coal power in the US still accounted for about 39% of the nation's

electricity production in 2014. (11). Even though a number of power plants have started replacing coal with natural gas, the combustion products still include NO_x species.

The emission of NO_x occurs due to the release of a flue gas mixture. This flue gas is typically composed of NO_x, SO_x and other trace metals such as mercury, lead, etc.

A typical coal fire power plant operates in 4 steps:

1) Heat is created: Coal is first made into powder and is then mixed with hot air that is blown into the combustion chamber. This coal/air mixture is burnt to provide complete combustion, and hence the maximum heat possible.

2) Water converted into steam: Water is pumped through the pipes and is turned into steam by the heat produced from combustion.

3) Steam drives the turbine: The pressure of the steam pushes against the turbine blades and causes them to rotate. The shaft of the turbine is connected to the shaft of the generator, where magnets spin within wire coils to produce electricity.

4) Steam is condensed: The steam is drawn into a condenser and is collected at cool water in the collection chamber. This water is then returned to its source and is used again to repeat the cycle. (12)

According to a report, the majority of the “coal dependent” states are in the eastern US. These states were termed “coal dependent” based on the frequency of appearance of these states in at least one or more, of the following six inclusion criteria:

- 1) Net expenditure on imported coal,
- 2) Net weight of imported coal,
- 3) Per capita spending on imported coal,
- 4) Spending on coal, relative to the size of the state economy,
- 5) Reliance on net coal imports relative to total power usage, and,
- 6) Total spending on international coal imports.

25 states were considered coal dependent with the leading states in the eastern US being Georgia, Alabama, Tennessee, Ohio, New Jersey, Connecticut and North Carolina (13).

Proposed Problem

The focus of this report is to assess an important air pollution problem and understand its sources. I found that coal fired power plants emit larger amounts of NO_x into the atmosphere relative to other emission sources such as vehicle exhaust. The emitted NO_x contributes to ozone and has negative effects on the climate and health. In the next chapter, the solution identification brief looks at various NO_x control methods and proposes a potential solution to reduce these emissions.

CHAPTER 2: SOLUTION IDENTIFICATION BRIEF

Introduction

This brief focuses on identifying the available NO_x control techniques and proposes a control method to further assess as a possible solution to reducing the NO_x emissions from coal fired power plants.

Historical attempts to reduce NO_x emissions

The first national cap and trade program was established in 1998, under the Clean Air Act amendments, called the Acid Rain Program (ARP). The purpose of the ARP was to reduce SO_x and NO_x emissions from the power sector, especially from Electrical Generation Units. Under the ARP, the NO_x reductions achieved were applicable only to a subset of coal fired power plants (14). In 2003, another cap and trade program was started with the goal of reducing the atmospheric transport of NO_x from power plants to other regions in the eastern United States, called the NO_x budget Trading Program (NBP). It was designed in addition to the ARP to further reduce NO_x emissions. The focus of the NBP was emissions during the summer season. In 2009, the NBP was replaced by a program under the Clean Air Interstate Rule (CAIR), which called for more stringent reductions of NO_x from power plants than the NBP. Every coal fire power plant was affected by these programs, which resulted in a noticeable reduction in the annual NO_x reductions (15).

Figure 1 shown below, is the annual NO_x trends from the CAIR, and the ARP sources from 1990 to 2013. It captures the decreasing trend in NO_x emissions over the years. The blue bars refer to the NO_x emissions from ARP, along with the CAIR units that were not in the ARP in 1990, 2000 and 2005; the 2008 NO_x emissions were applied retroactively for each pre-CAIR year after which the CAIR units began operation. The orange bars refer to both, the ARP and CAIR sources together. Green bars refer only to ARP sources, and the yellow bars refer to the

CAIR sources, exclusively. The dotted line represents the NO_x annual budget for the CAIR program (approximately 1.3 million tons of NO_x)- this was the final cap that the program was set to achieve by 2015.

The NO_x emissions are shown in the form of stacked bars to highlight the contribution of each program to the total reduction in NO_x emissions from the CAIR and ARP sources.

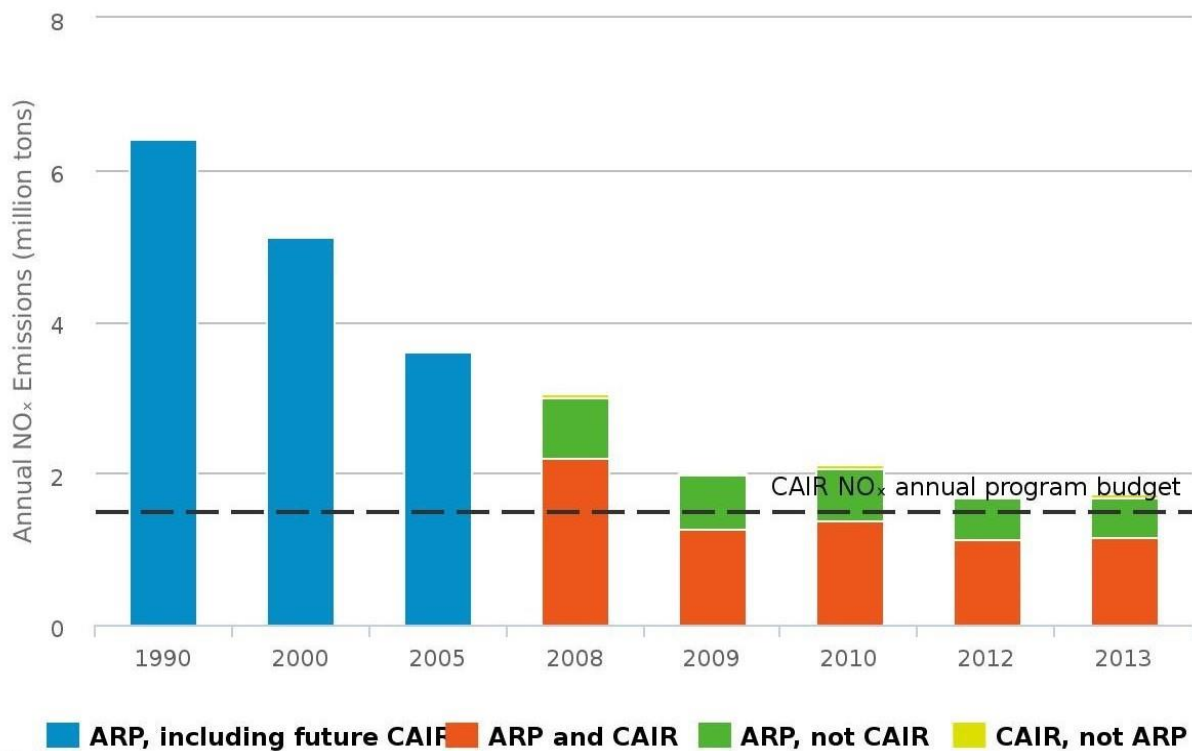


Figure 1. Annual NO_x emissions from CAIR and ARP sources [15]. Blue refers to the ARP and retroactively-fit CAIR sources. The orange bars refer to both ARP and CAIR sources combined together. The green and yellow bars refer individually to ARP and CAIR sources. The dotted line represents the annual NO_x budget for CAIR (approximately 1.3 million tons of NO_x).

Available NO_x control techniques

NO_x emissions can be controlled by either implementing pre-combustion controls or post-combustion controls, or a combination of both. Traditional methods of emission controls

involve pre-combustion controls such as Staged combustion and Reburning. Staged combustion aims to efficiently curb the amount of NO_x going through the combustion chamber. It uses the remaining air for complete combustion, as “overfire air”, which is the secondary air introduced into the furnace. Doing this results in a reduced amount of air in the combustion zone. This type of a combustion system NO_x control is generally the least costly approach relative to other methods such as Reburning, but may lack the efficiency to meet the required emissions.

Reburning is a process which aims to decompose the NO_x formed during the initial combustion cycle. It involves the addition of a supplemental fuel, typically natural gas, for further burning to occur. This results in some of the NO_x being converted back to molecular nitrogen.

Another pre-combustion method of regulating NO_x emissions is to use Low-NO_x burners (LNB). These burners have a lower intake of air within the combustion chamber, which creates a fuel-rich zone. This also lowers the temperature of the operation. Both these factors, the fuel-rich atmosphere and the lowered temperature lead to reduced formation of NO_x. The remaining air is then re-used as overfire air to incorporate reburning (16).

In addition to these NO_x control measures, there are a number of other technologies and methods that can be implemented. Wet scrubbing is a post-combustion technique that is used to remove or “filter” the gases from a flue gas stream. It involves the use of a scrubbing liquid to absorb or dissolve the pollutant from the exhaust stream. Though there are many types of wet scrubbers, the primary purpose is to collect and filter out both particulate and gaseous pollutants within the system. Wet scrubbing technology has the advantage of being very flexible; there are many variations of wet scrubbers. The disadvantage however, is that it creates a large amount of liquid waste (17).

Another pre-combustion control technology involves the use of a catalyst. It is of two types, namely: Selective Catalyst Reduction (SCR) and Selective Non Catalyst Reduction (SNCR). The SCR approach involves the injection of a reducing agent such as urea and ammonia, which converts the nitrogen oxides in the exhaust stream to diatomic nitrogen and water. Relative to the traditional methods, the biggest advantage of the SCR control technology is lowered operation costs. Consequently, the disadvantages for this technology are high equipment cost, high operating temperature, and increased production of particulates (18).

SNCR uses a similar approach as the SCR method, but does not involve the use of a catalyst. Either ammonia or urea is injected directly into the flue gas stream where they react with the NO_x compounds to form diatomic nitrogen and water. This approach has an economic advantage over the SCR and achieves about the same efficiency as that of the SCR. The disadvantages of SNCR however, involve the constraints of time, mixing and an optimal temperature range (18).

An alternative pre-combustion approach is to use biomass-coal co-combustion. These biomasses include herbaceous and wood fuels, as well as residues from crops. Addition of biomass to a coal-boiler vessel does not significantly affect the overall efficiency of the plant; at worst, it only slightly decreases the efficiency. Although biomass cofiring is slightly more expensive than coal-only systems, it offers the benefit of a CO₂-neutral energy. Additional benefits are low-risk, abundance of biomass-fuel and improved overall grid-management. The biggest shortcomings, however, are the availability of indigenous biomass fuel and transport, ash deposition and corrosion. When the proper choices of biomass, coal, boiler design and boiler operations are made, traditional pollutants, such as (NO_x, SO_x etc.), and net greenhouse gases (such as CO₂, CH₄, etc.) emissions decrease (19).

Another post-combustion control technology is the oxy-fuel combustion technology. This approach replaces the traditionally used air with pure oxygen. This combustion technology

recycles the flue gas back to the combustion chamber to control the temperature and make up for the missing diatomic nitrogen gas. This ensures that there is enough volume of gas to carry the heat through the boiler. Advantages of this approach include increased efficiency and its application as a retrofit technology to a plant. A big disadvantage, however, is that it can result in unpredictable heat transfer and combustion patterns (20).

An alternative approach being explored in the research community is the use of an Electricity Grid Management model (EGM). This approach combines a three-dimensional air quality model such as the Comprehensive Air Quality model (CAMx) with a model of the daily management of the electricity grid (21). This dynamic management system would focus on days with air pollution concentrations exceeding the daily standards and the geographical scope of the analysis. The air quality modeling domain will roughly match the electric grid modeling domain. The CAMx model will be run for a selected historical episode of an exceedance of the 8-hour ozone standard, to find contributions of EGUs to ozone. Decision rules will then be tested for a regional electric dispatch model. These decision rules will help determine the decrease needed in generation at power plants, which are significantly influencing the ozone peak. The management system will make use of the decision rules to modify emissions from power plants by shifting the electricity generation to other power plants so as to reduce ozone. The CAMx model will be rerun with new power plant emissions to evaluate the efficacy of these decision rules. Though individual power plants may have operation limitations and other constraints on annual emissions, currently, the grid by itself, does not implement air-quality limits in any manner. In addition to potentially meeting the daily ozone air quality standards at a low cost, the biggest strength of this approach is that the adjustment of controls and decisions of the electricity generation units can be made from nearly anywhere in the country. The EGM model also accounts for uncertainty in the ozone peaks due to NO_x. This makes the EGM approach into an adaptive and effective NO_x control technique. The downside of this approach,

however, is its reliance on the errors within the air quality forecast models and the possibility of false-positive or false-negative projections. It also may reduce its effectiveness and lead to increased costs. An added disadvantage is the increased system costs and decreased efficiency of the electricity-system operations when adjusting the generator dispatch in response to predicted air-quality events.

Proposed Solution

Most of the NO_x control measures deal with tradeoffs between the implementation cost and the efficiency of these measures. Most of the NO_x control technologies incur an additional expenditure as they involve usage of substances such as catalysts, natural gas, etc. The EGM model, however, does not involve the use of any such substances. Hence, incorporating the EGM model within coal-fired power plants may be a better option as it has the potential to meet daily ozone air quality standards at a low cost. By improving air quality, this approach would offer benefits for both the public health, as well as that of the environment (21).

CHAPTER 3: IMPLEMENTATION BRIEF

Description of dataset

Characterization of the impact of ozone precursor emissions from coal fired power plants was done using the CAMx model data of the summer season of 2005 (June 28th to August 23rd, 2005). The model inputs were developed by the EPA for a base-case simulation, for its analysis of the final Transport Rule. This also included refined meteorological and emissions fields for 2005, across the eastern United States (21).

The data pertains to the 80 coal fired power plants in the eastern US. Of all the modelling days, August 4th and August 13th, were chosen as they were known to have a high ozone episode on both those days- 81.6ppb and 81.0ppb (21). Figure 2 shown below represents the number of grid cells from the model runs for all the 56 days that exceeded the 70ppb limit of ozone.

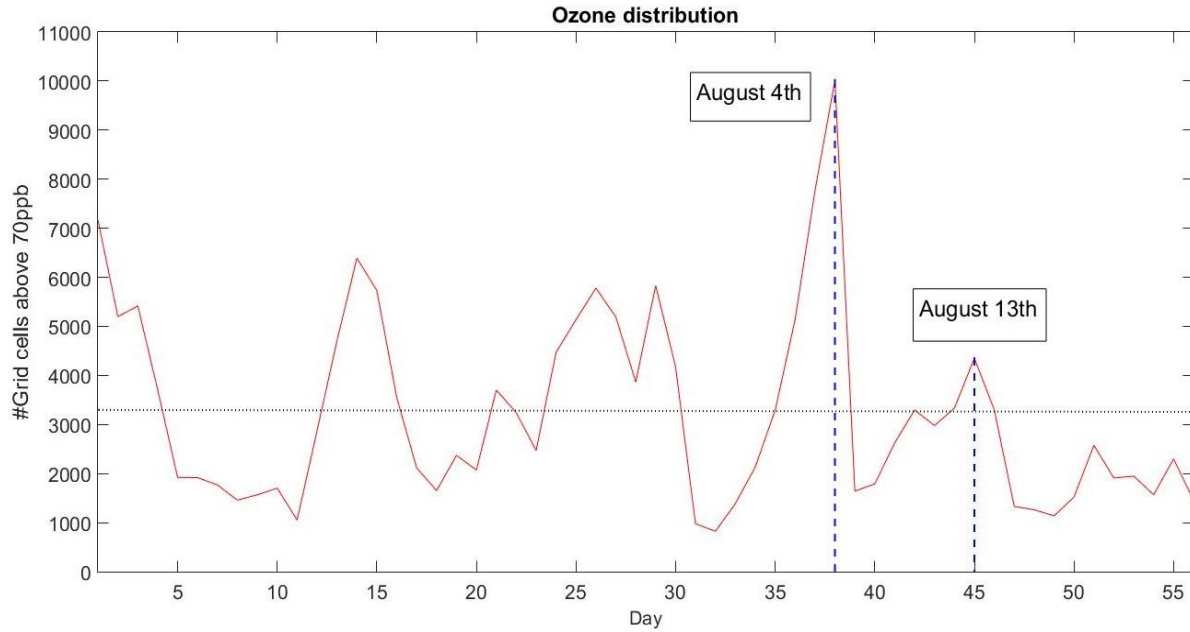


Fig 2. Number of grid cells from outputs of the brute force runs, exceeding the 70ppb limit. The lines marked in blue represent the two days of interest, August 4th and August 13th. The black dotted line represents the average number of grid cells exceeding 70ppb, which is the current EPA standards for ozone.

The blue lines in figure 2 mark the two days of interest that were chosen- August 4th and August 12th. The black dotted line shows the average number of grid cells that exceeded 70ppb for each of these days (approximately 3240 grid cells). August 4th is somewhat of an extreme case, with more than 10,000 grid cells exceeding 70ppb. On the other hand, August 13th is more representative of an average case, with approximately 4400 grid cells exceeding 70ppb.

ΔOzone plots for 24 hour zero out runs

Brute force is a type of sensitivity technique that was used to quantify the sensitivity of high ozone to NOx emissions. In this study we will zero out the NOx emissions 24 hours prior to the start of August 4th and August 13th. All the delta ozone plots were generated by subtracting the base case from the sensitivity case, or the brute force simulation. The “base case” refers to all the ozone precursor emissions including the ones from the coal fired power plants, and the

“sensitivity case” or “sens case” refers to all the ozone precursor emissions except the ones from coal fired power plants.

Therefore, a negative ozone value implies a reduction in the ozone levels, and a positive value implies an increase in ozone levels. Figures 3a and 3b show the maximum decrease and maximum increase in ozone levels for the 24 hr zero out run on August 4th.

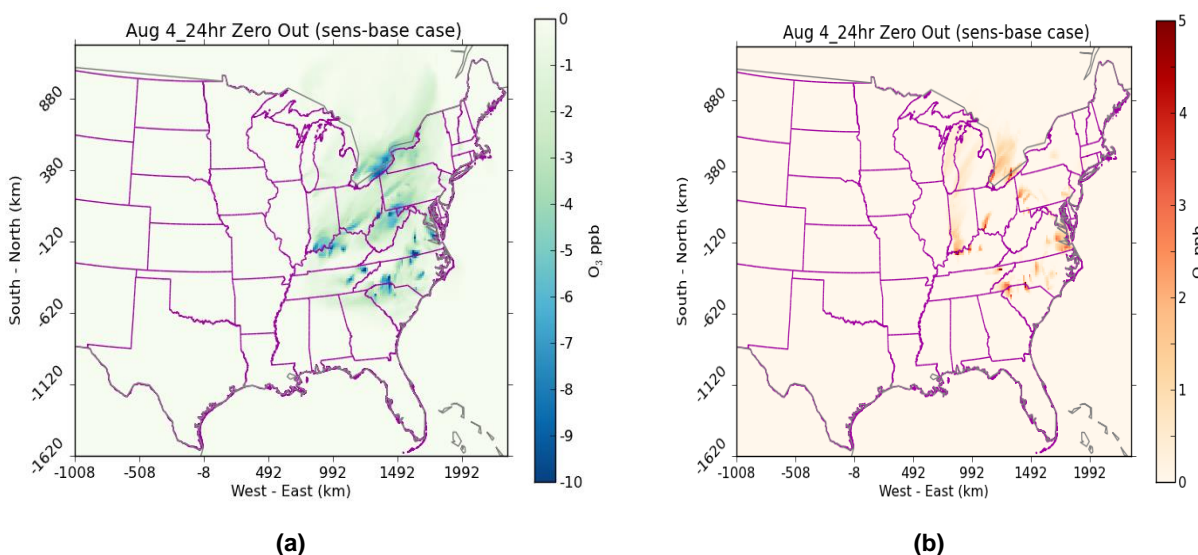


Fig 3. Δ Ozone plots (sens-base case) in ppbV for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in hourly ozone concentrations for August 4th, regardless of the hour.

In the maximum decrease plot for August 4th (fig. 3a), there are reductions ranging from 1 ppb to more than 6ppb, in the majority of the locations. In certain locations such as Knoxville and Cincinnati, there are large reductions in ozone levels (more than 10ppb). The maximum decrease observed (approximately 19ppb) was in the southern part of Virginia.

In the maximum increase plot for August 4th (fig. 3b), there are increases in ozone levels ranging between 1ppb and 4ppb, in most locations. There are certain locations, however, such as Knoxville and Charlotte that experienced the highest increase in ozone levels- up to 8ppb.

Figure 4 below, represents a box and whisker plot of the 24 hour zero-out run for August 4th. The changes in ozone levels within a day are seen in these figures. The box and whisker plot also is generated using a sens-base case approach, but shows only the temporal aspect; it is irrespective of the spatial domain.

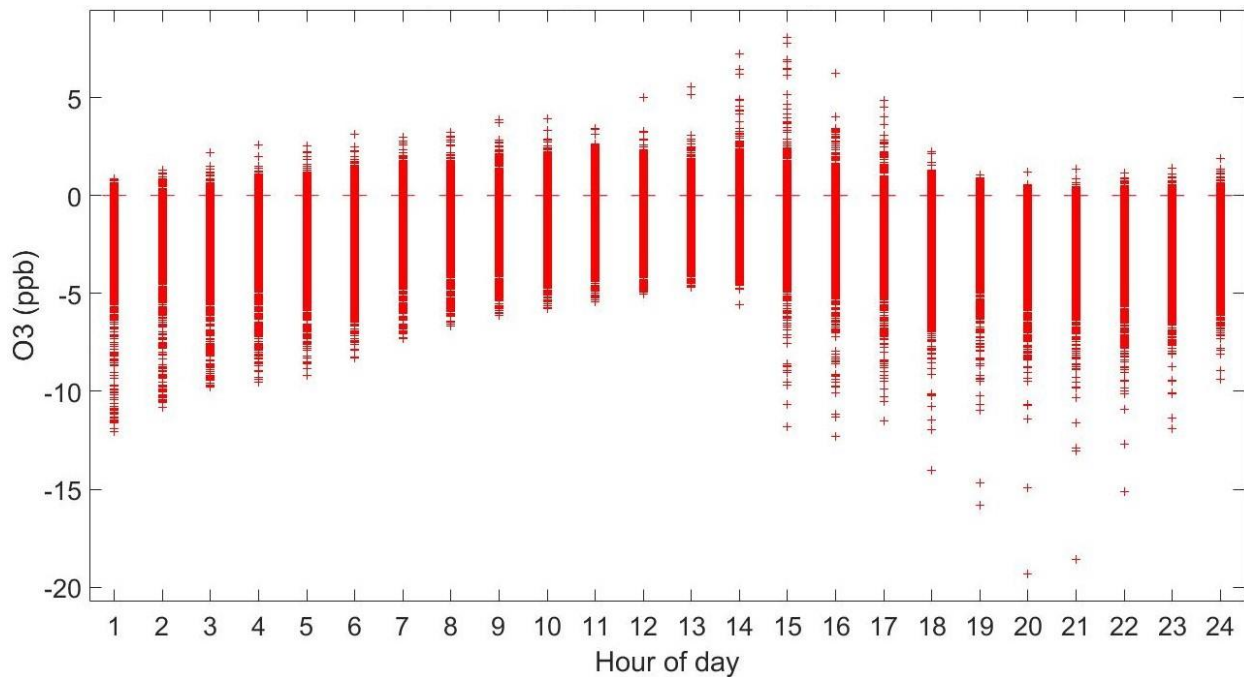


Fig 4. Box and whisker plot for the 24 hr zero out run (base-sens case), on August 4th. The figure shows the increase and decrease in ozone levels over time. The plot only shows the temporal aspect; it does not consider the spatial domain.

The box and whisker plot shows the change in ozone levels with respect to time (up to 24 hours). There is a gradual decrease in the reduction of ozone levels (negative values) up to the 14th hour, after which, there is an increase in the ozone levels through the evening and the night period. The amount of ozone being produced also gradually increases until noon (hour 15) after which there is a drop in the amount of ozone produced during the evening and night times.

Figures 5a and 5b below, show the maximum decrease and maximum increase in ozone levels for the 24 hr zero out run on August 13th.

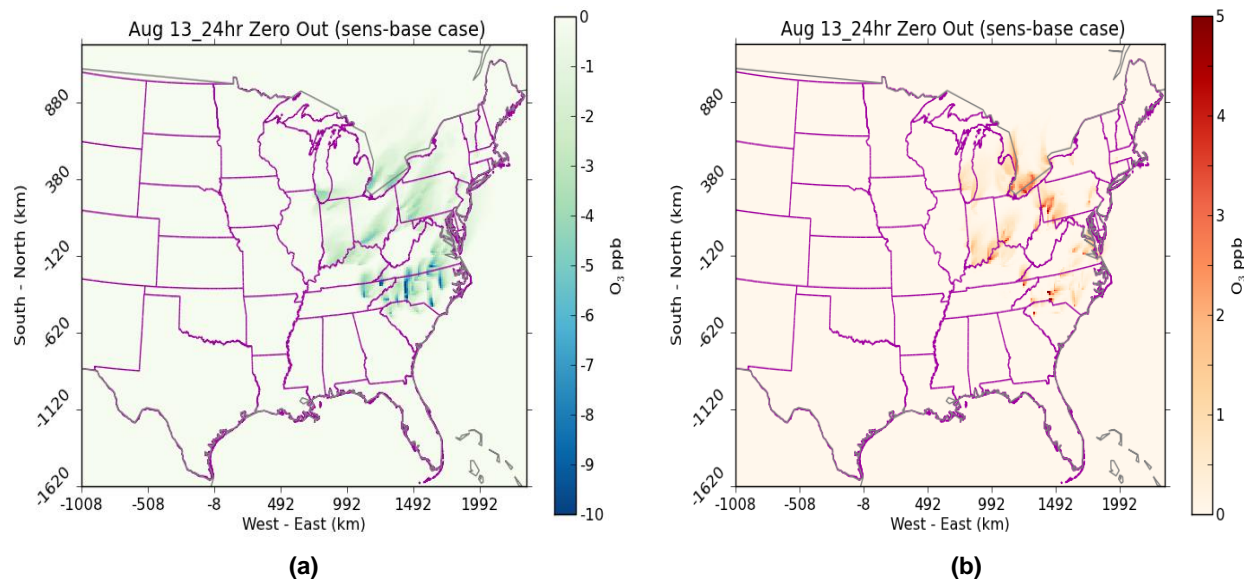


Fig 5. Δ Ozone plots (sens-base case) in ppbV for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in hourly ozone concentrations for August 13th, regardless of the hour.

In the maximum decrease plot for August 13th (fig. 5a), for the majority of the locations, the reductions in ozone levels range between 1ppb and 5ppb. But for certain areas such as Charlotte and Knoxville, there are reductions in ozone levels more than 10ppb. The maximum reduction in ozone (approximately 20ppb) was seen in Charlotte.

In the maximum increase plot for August 13th, (fig. 5b), there are increases in ozone levels ranging between 1ppb and 4ppb, in most locations. There are certain locations, however, such as Cincinnati and Charlotte which experienced the highest increase in ozone levels- up to 22ppb.

Figure 6 below, represents a box and whisker plot of the 24 hour zero-out run for August 13th. The changes in ozone levels within a day are seen in these figures.

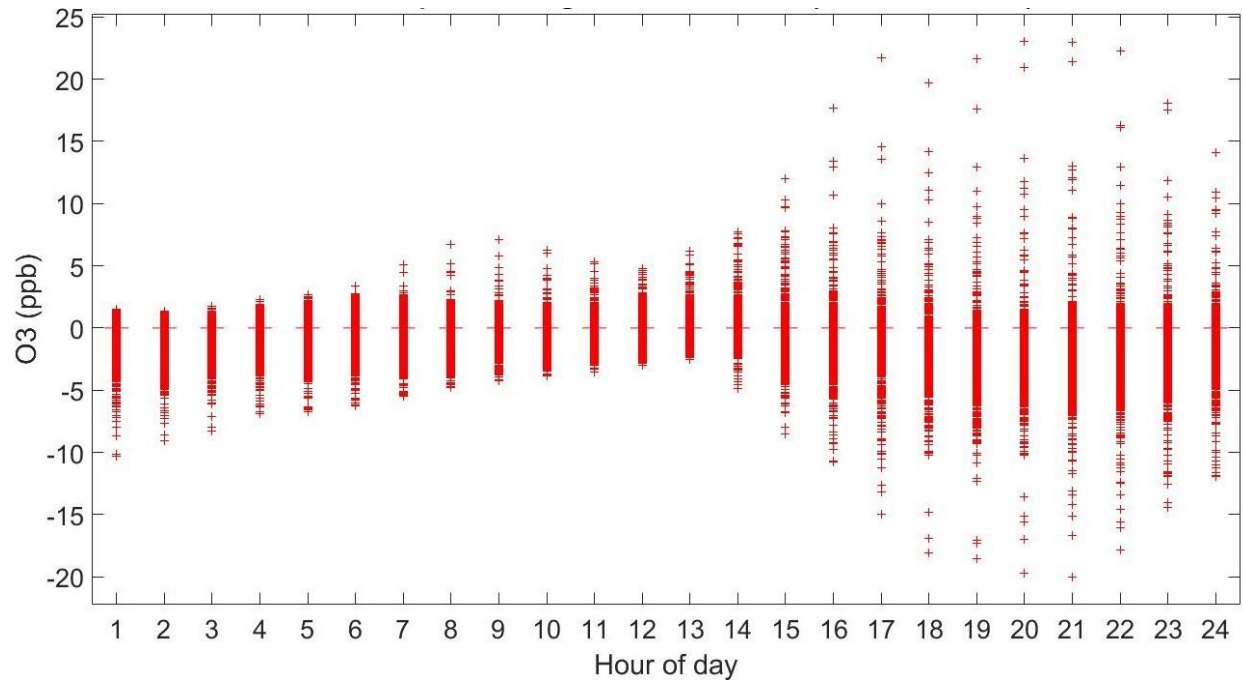


Fig 6. Box and whisker plot for the 24 hr zero out run (base-sens case), on August 13th. The figure shows the increase and decrease in ozone levels over time. The plot shows only the temporal aspect; it does not consider the spatial domain.

Positive ozone values imply a production in ozone, while the negative values imply a reduction in ozone. The box and whisker plot shows the change in ozone levels with respect to time (up to 24 hours). There is a gradual decrease in the reduction of ozone levels (negative values) up to noon (hour 13), after which, there is an increase in the ozone levels through the evening and the night period.

The amount of ozone being produced for August 13th, however, has a different trend as compared to the one for August 4th. The ozone production for August 4th increased until the afternoon time (hour 15) and then gradually decreased. But, for August 13th, the amount of ozone produced increases even after the noon time (hour 15).

Of all the coal fired power plants in and around the region, the top 6 facilities had a major contribution toward the overall NO_x emissions (21). Focusing on these coal fired power plants is easier and can contribute to a significant reduction in the ozone levels.

Nonattainment areas

Nonattainment areas are regions that have exceeded the ozone standards as set by the EPA. Figure 7 below, shows the 8-hour ozone nonattainment area map for the year 2008.

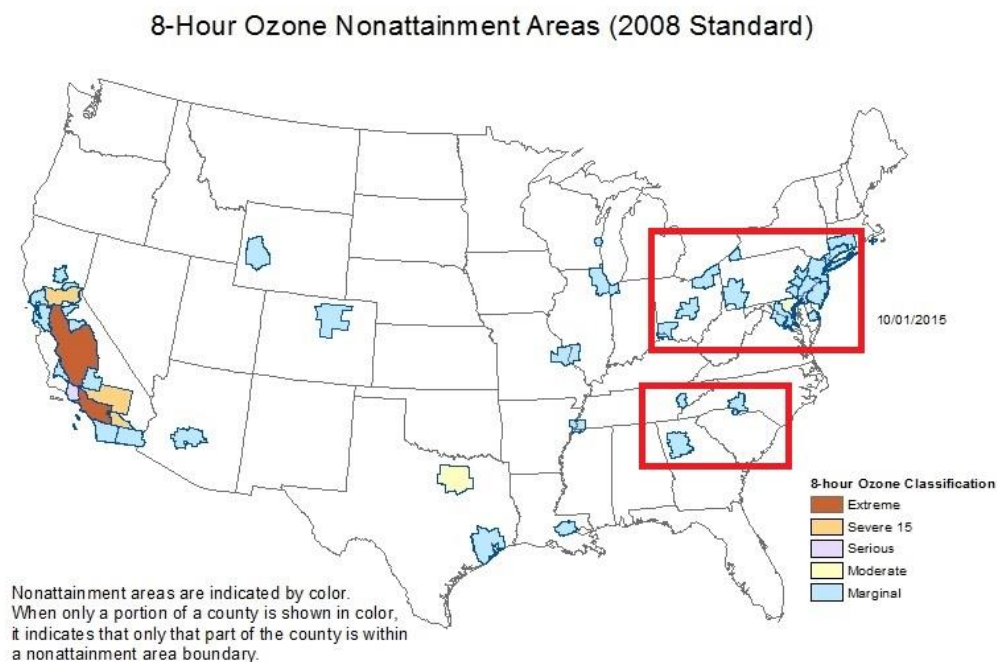


Fig 7. Nonattainment area Map, 2008 standard [22]. Two groups of nonattainment areas are marked in red. Group 1 consists of New York, New Jersey, Maryland, Connecticut, Pittsburgh, Cleveland, Columbus and Cincinnati. Group 2 consists of Charlotte, Atlanta and Knoxville.

To see how these nonattainment areas were impacted by the change in ozone levels, the 24 hr zero out run for August 4th and August 13th, were mapped over these areas. The nonattainment areas were divided into two groups, as marked in figure 7. Group 1 included

Pittsburgh, New Jersey, New York, Connecticut, Massachusetts, Cleveland, Columbus and Cincinnati. And group 2 consisted of Charlotte, Atlanta and Knoxville.

Figures 8a and 8b below, show the maximum decrease and maximum increase in ozone levels over Group 1 for August 4th.

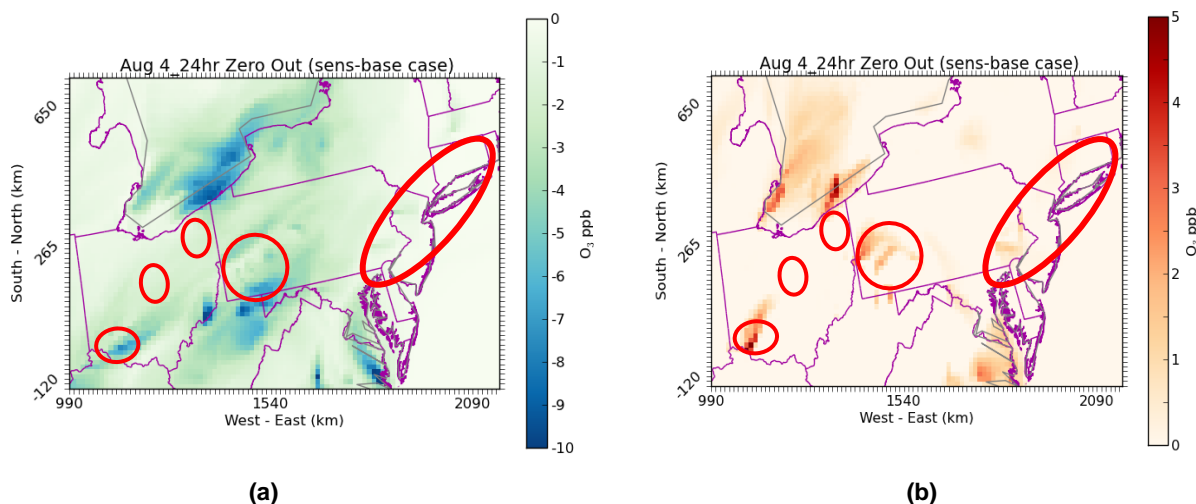


Fig 8. Δ Ozone plots (sens-base case) for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in ozone levels for August 4th over the nonattainment areas marked as group 1. The areas consist of New York, New Jersey, Maryland, Connecticut, Pittsburgh, Cleveland, Columbus and Cincinnati.

In the maximum decrease plot for group 1 (fig. 8a), Pittsburgh and Cincinnati have reductions in ozone levels of up to 6ppb. Cleveland and Columbus have reductions in ozone levels up to 3ppb. Except for a few areas with up to 2ppb reduction in ozone, the New Jersey, New York area does not experience any significant reductions.

In the maximum increase plot for group 1 (fig. 8b), Cincinnati has the highest increase in ozone levels, going up to 5ppb. The other regions, such as Pittsburgh, Cleveland, Columbus, New York, New Jersey, etc. experience increases in ozone levels ranging between 1ppb and 3ppb.

Figures 9a and 9b shown below, represent the maximum decrease and maximum increase over Group 2 for August 4th.

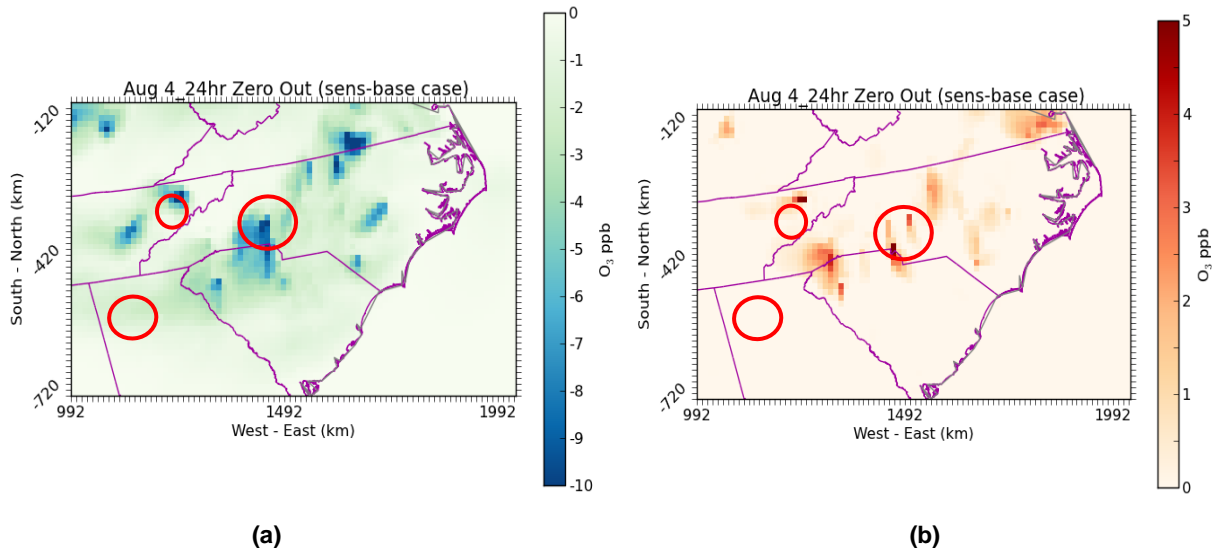


Fig 9. Δ Ozone plots (sens-base case) for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in ozone levels for August 4th over the nonattainment areas marked as group 2. The areas consist of Charlotte, Atlanta and Knoxville.

In the maximum decrease plot for group 2 (fig. 9a), Charlotte and Knoxville have reductions in ozone levels up to 10ppb. Atlanta experiences reductions in ozone levels ranging between 1 and 3ppb.

In the maximum increase plot for group 2 (fig. 9b), Charlotte has increases in ozone levels of up to 5ppb. Knoxville and Atlanta, experience increases in ozone levels ranging between 1 and 2ppb.

Figures 10a and 10b shown below, represent the maximum decrease and maximum increase over Group 1 for August 13th.

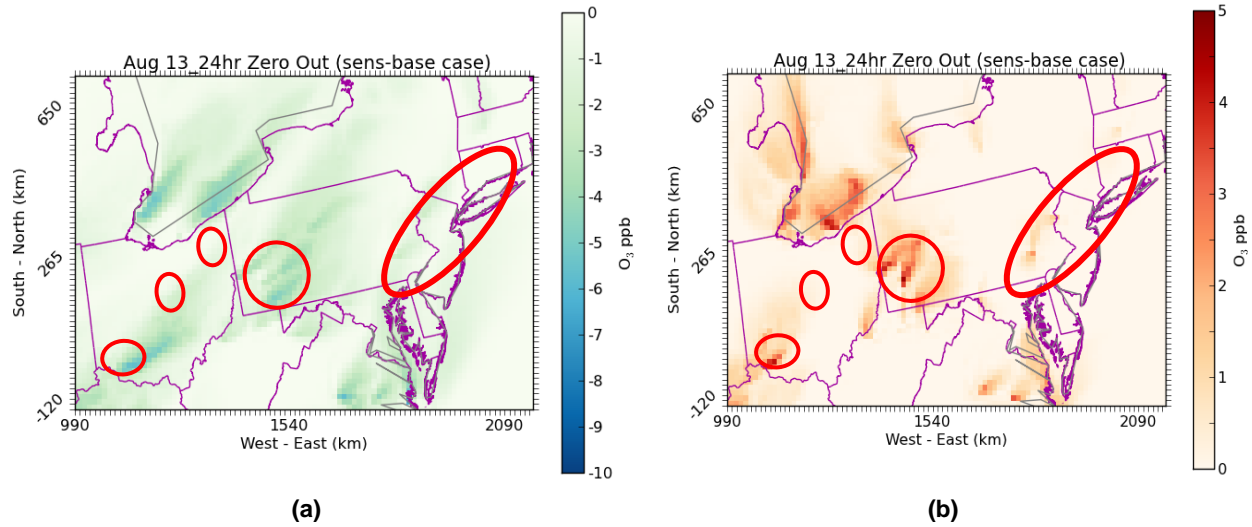


Fig 10. Δ Ozone plots (sens-base case) for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in ozone levels for August 13th over the nonattainment areas marked as group 1. The areas consist of New York, New Jersey, Maryland, Connecticut, Pittsburgh, Cleveland, Columbus and Cincinnati.

In the maximum decrease plot for group 1 (fig. 10a), Pittsburgh and Cincinnati have reductions in ozone levels of up to 6ppb. Cleveland and Columbus have reductions in ozone levels up to 3ppb. Except for a few areas with up to 2ppb reduction in ozone, the New Jersey, New York area does not experience any significant reductions.

In the maximum increase plot for group 1 (fig. 10b), Cincinnati has the highest increase in ozone levels, going up to 22ppb. Pittsburgh has increases in ozone levels, going up to 6ppb. The other regions, such as Cleveland, Columbus, New York, New Jersey, etc. experience increases in ozone levels ranging between 1ppb and 3ppb.

Figures 11a and 11b shown below, represent the maximum decrease and maximum increase over Group 2 for August 13th.

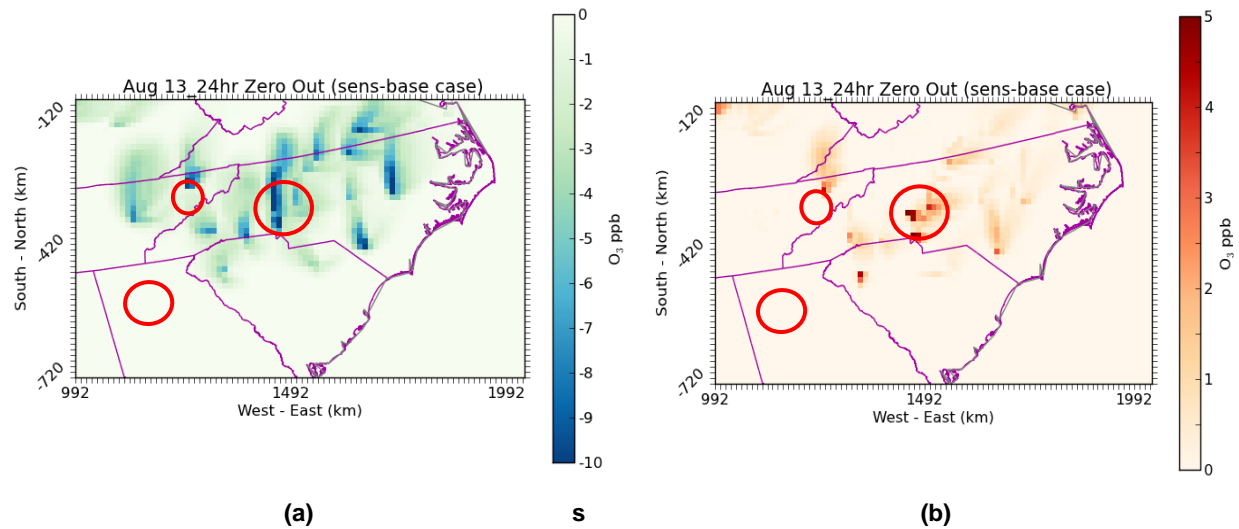


Fig 11. Δ Ozone plots (sens-base case) for the 24 hr zero out run, showing (a) maximum decrease and (b) maximum increase in ozone levels for August 13th over the nonattainment areas marked as group 2. The areas consist of Charlotte, Atlanta and Knoxville.

In the maximum decrease plot for group 2 (fig. 11a), Charlotte has a maximum reduction in ozone levels, going up to 20ppb. Only the northern part of Knoxville has reductions in ozone levels, going up to 10ppb. Atlanta has no significant reductions in ozone levels.

In the maximum increase plot for group 2 (fig. 11b), Charlotte has the largest increase in ozone levels of up to 22ppb. Knoxville and Atlanta, do not experience any significant increases in ozone levels.

Conclusions

Coal fired power plants impact ozone significantly, as estimated through brute force sensitivity. Reductions in the ozone precursor emissions due to the power plants, generally ranged between 1ppb and 6ppb, but in specific locations, exceeded 10ppb. There were increases in ozone precursor emission levels ranging between 1ppb and 4ppb for most

locations, but in certain locations, exceeded 10 ppb. Nonattainment areas have reductions in ozone levels of up to 6ppb for most locations. For certain locations, such as Charlotte, the maximum reduction in ozone levels was approximately 20ppb. Increases in the ozone levels for most nonattainment areas ranged between 1ppb and 5ppb. Certain nonattainment areas such as Charlotte and Cincinnati experienced the maximum increase in ozone levels, going up to 22ppb. Although both days had a similar behavior in ozone reduction levels, August 13th experienced a much larger increase in the ozone levels than August 4th. Though the increases in ozone levels may be a problem for the regulators, they can make use of the predictions from the CAMx model to take suitable measures in anticipation of predicted high ozone episodes. The reductions can be very beneficial in helping the nonattainment areas meet the required ozone air quality standards. Most of the NOx control technologies operate using substances such as catalysts, natural gas, etc., which translate into additional expenditure. The EGM model is not subject to such expenditures as it does not involve the use of any such substances. The EGM model has the potential to meet the daily ozone air quality standards at a low price. Future work should investigate the chemical or physical mechanisms which may be responsible for the increased levels of ozone.

REFERENCES

- 1) Rubin, M. B.: The history of ozone. The Schonbein period, 1939– “ 1868., Bull. Hist. Chem., 26, 40–56, 2001.
- 2) Le Tertre A, Medina S, Samoli E, et al. Short-term effects of particulate air pollution on cardiovascular diseases in eight European cities. J Epidemiol Community Health 2002;56:773–9.
- 3) Kelly FJ, Oxidative stress: its role in air pollution and adverse health effects. Occup Environ Med 2003;60:612–16.
- 4) Henrotin JB, Besancenot JP, Bejot Y, Giroud M. Short-term effects of ozone air pollution on ischaemic stroke occurrence: a case-crossover analysis from a 10-year population-based study in Dijon, France. Occup Environ Med 2007;64:439 – 445.
- 5) Jerrett M, Burnett RT, Pope CA 3rd, et al. Long-term ozone exposure and mortality. N Engl J Med 2009; 360: 1085–95.
- 6) Stevenson DS, Dentener FJ, Schultz MG, et al. Multimodel ensemble simulations of present-day and near-future tropospheric ozone. J Geophys Res 2006; 111. DOI:10.1029/2005JD006338.
- 7) EIA, US. 2013. Annual energy outlook 2013. Energy Information Administration, US Department of Energy: Washington, DC www.eia.gov/forecasts/aeo, Accessed on 25-November, 2015.
- 8) EIA, US. 2012. Annual energy review 2011. Energy Information Administration, US Department of Energy: Washington, DC www.eia.doe.gov/emeu/aer, Accessed on 25-November, 2015.
- 9) EPA, US. 2011a. Air Emission Sources. Accessed on 25- November, 2015.
- 10) Kim, S.-W., Heckel, A., McKeen, S.A., Frost, G.J., Hsie, M.K., Trainer, M., Richter, A., Burrows, J., Peckham, S.E., Grell, G., 2006. Satellite-observed US power plant NO_x emission reductions and their impact on air quality. Geophysical Research Letters 33, L22812.
- 11) EIA, US. 2014. Annual power generation. Energy Information Administration, US Department of Energy: Washington, DC www.eia.gov/forecasts/aeo, Accessed on 25-November, 2015.

- 12) Duke Energy, How do coal-fired plants work. <https://www.duke-energy.com/about-energy/generating-electricity/coal-fired-how.asp>, Accessed on 25-November, 2015.
- 13) UCS, 2010, Burning Coal, Burning Cash, http://www.ucsusa.org/clean_energy/smart-energy-solutions/decrease-coal/burning-coal-burning-cash.html#.VIXx0_mrShc, Accessed on 25-November, 2015.
- 14) EPA, US. Acid Rain Program. <http://www.epa.gov/airmarkets/acid-rain-program>, Accessed on 30-January, 2016.
- 15) EPA, US. NOx Budget Trading Program. <http://www.epa.gov/airmarkets/nox-budget-trading-program>, Accessed on 30- January, 2016.
- 16) Clean Coal Technology. Reducing Emissions of Nitrogen Oxides via Low-NOx Burner Technologies, <https://www.netl.doe.gov/File%20Library/Research/Coal/major%20demonstrations/cctdp/Round3/topical5.pdf>, Accessed on 30- January, 2016.
- 17) Products Finishing, 2014. NOx Scrubbing Technology Breakthrough. <http://www.pfonline.com/articles/nox-scrubbing-technology-breakthrough>, Accessed on 30-January, 2016.
- 18) Gullett, B.K., Groff, P.W., Lin, M.L., Chen, J.M., 1994. NOx removal with combined selective catalytic reduction and selective noncatalytic reduction: pilot-scale test results. J. Air Waste Manage. Assoc. 44, 1188–1193.
- 19) L. Baxter, Biomass-coal co-combustion: opportunity for affordable renewable energy, Fuel 84 (10) (2005) 1295–1302.
- 20) Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF. Oxy-fuel combustion technology for coal-fired power generation. Progress in Energy Combust Science 2005;31(4):283-307.
- 21) Couzo, E., J. McCann, W. Vizuete, S. Blumsack, and J. J. West. "Modeled Response of Ozone to Electricity Generation Emissions in the Northeastern US Using Three Sensitivity Techniques." Journal of the Air & Waste Management Association (1995) (2016).
- 22) EPA, US. Green Book Nonattainment Areas, 8-Hour Ozone (2008). https://www3.epa.gov/airquality/greenbook/map8hr_2008.html, Accessed on 3- April, 2016.